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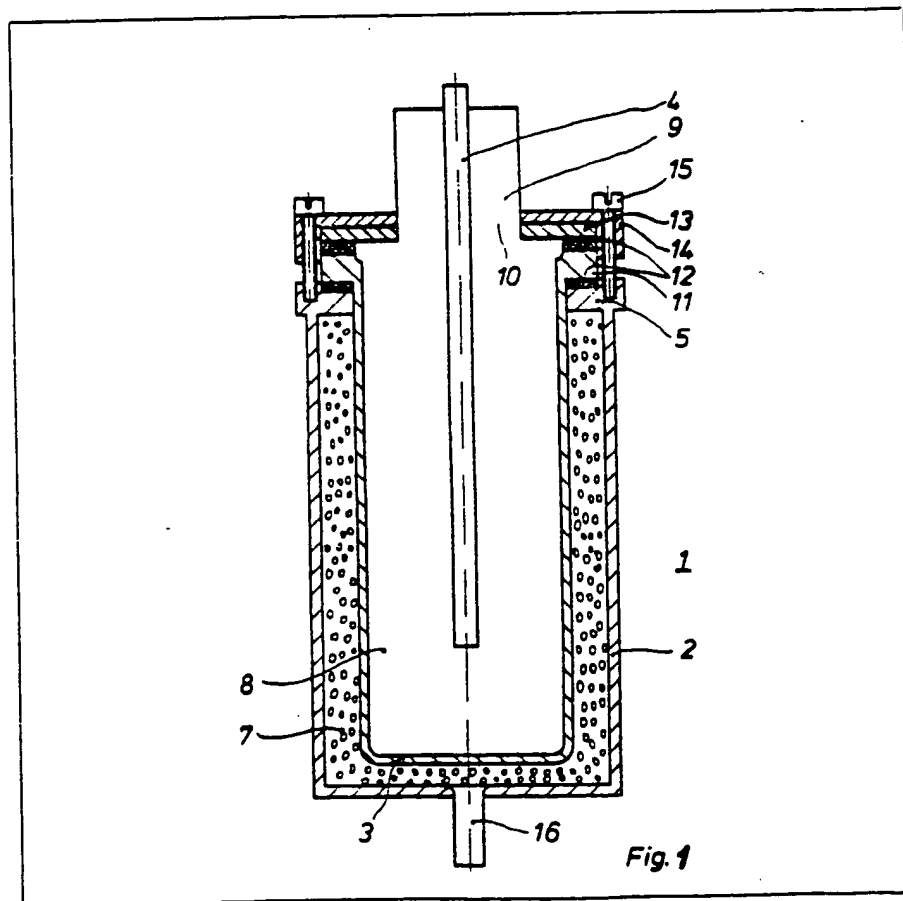
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(54) Electrochemical storage cell

(57) The invention relates to a storage cell of the alkali metal/chalcogen type having anode and cathode compartments for the anolyte and catholyte respectively and an additive in the cathode compartment to reduce internal resistance and improve recharging, the additive being a mixture of expanded graphite and sulphur, preferably in the ratio of 85% sulphur to 15% graphite by weight.



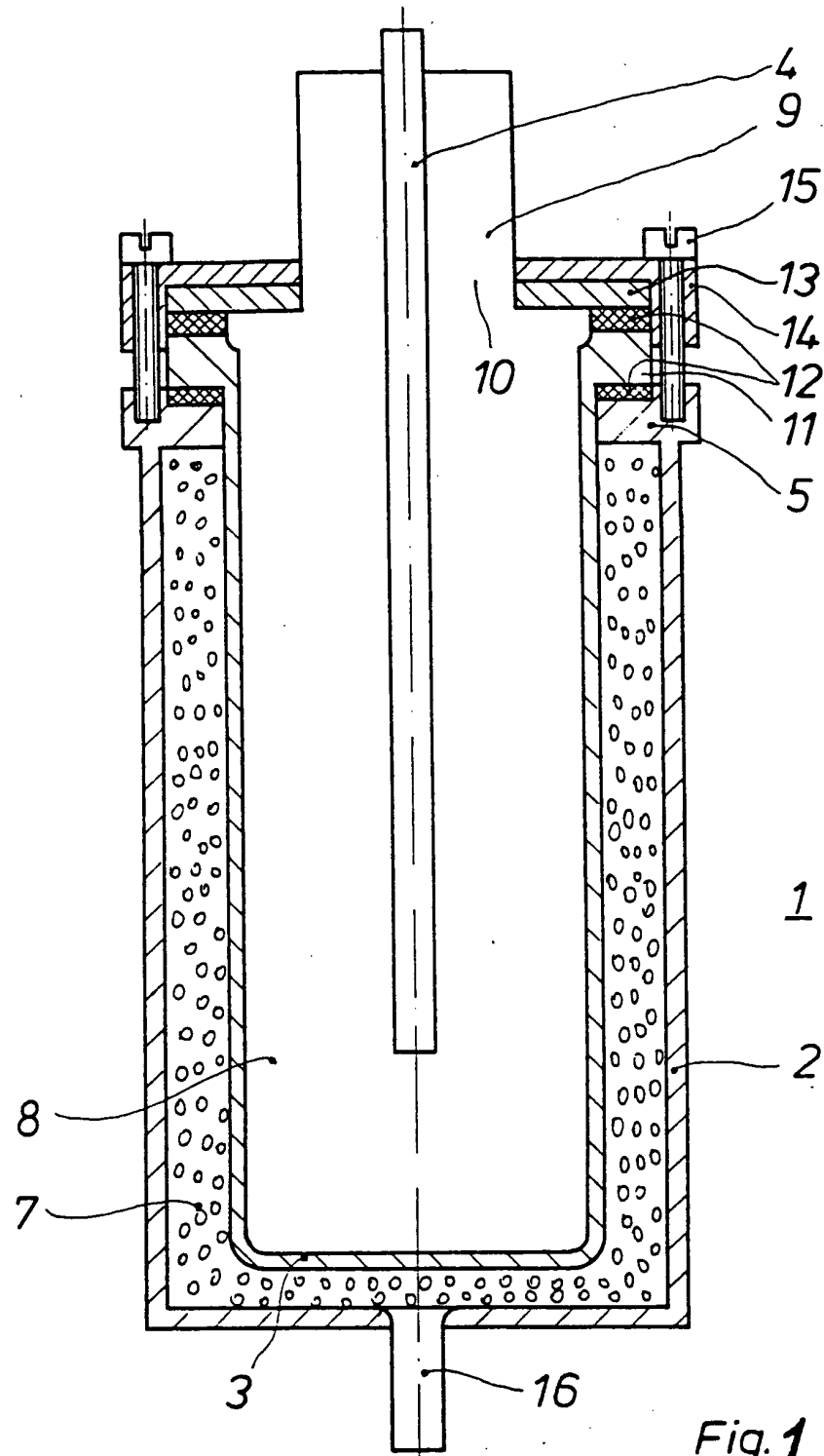


Fig. 1

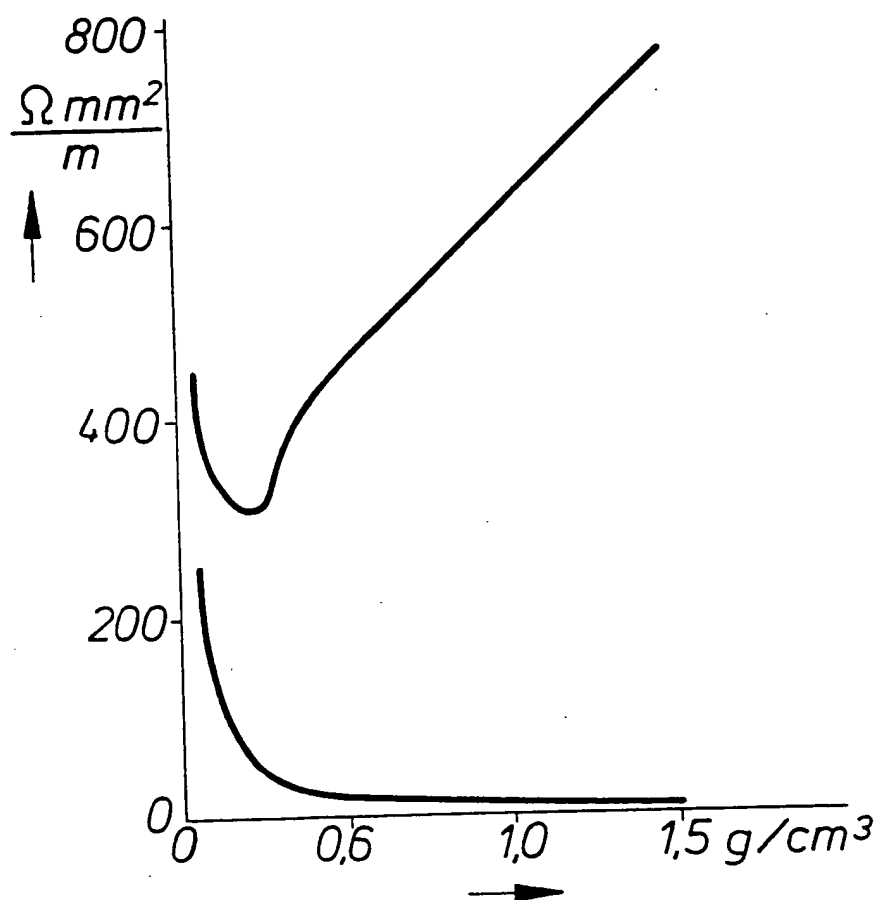


Fig. 2

SPECIFICATION

Electrochemical storage cell

- 5 The invention relates to an electrochemical storage cell or battery based on alkali metal and chalcogen, comprising at least one anode compartment for holding the anolyte and a cathode compartment for holding the catholyte, these being separated from each other by an alkali ion-conducting solid electrolyte wall, an additive being placed into the cathode compartment for reducing the internal resistance and increasing the electrochemical reaction.
- 10 Such rechargeable electrochemical storage cells with solid electrolytes are very suitable for forming accumulators of higher energy and power density. The beta aluminium oxide electrolyte used for example in sodium/sulphur storage cells allows only sodium ions to pass. In contrast to the lead accumulator, this means that practically no self discharge takes place, and no termination of charging there are no secondary reactions such as water decomposition in the case of the lead/lead oxide system. The current yield, i.e. the Faraday efficiency, of a sodium/sulphur storage cell is 100%.
- 15 However, a substantial drawback of such a storage cell is that it can only be partly recharged with large currents. This drawback is connected with the fact that in Na/S storage cells, sulphur (containing small proportions of dissolved Na_2S_3) and Na_2S_5 (containing proportions of dissolved sulphur) from two immiscible fluids at the operating temperatures of such a storage cell, i.e. 300 to 350°C. In this respect, if a discharged Na/S storage cell containing Na_2S_3 in the cathode compartment is again charged, sulphur-rich sulphides firstly form until Na_2S_5 is present in the entire cathode compartment or at least locally. As charging continues, liquid sulphur forms at positions of high electrochemical conversion, and this acts as an insulator to block the electrochemical processes at these positions.
- 20 In order to obviate this drawback, as shown from DE-OS 2 207 129, the cathode compartment may be filled with a felt made of graphite or carbon, the felt being impregnated with sulphur during the manufacture of the cell. The graphite felt serves to increase the surface area necessary for the electrochemical reaction, between the sulphur or the alkali sulphide arising during discharge and the cathode collector, the felt being seen as an extension of this latter. In addition, by this means the distance between the solid electrolyte and the thus extended cathode current collector becomes smaller, so that the resistance of the sulphur or sodium polysulphide contributes less to the internal resistance of the cell.
- 25 A drawback of storage cells which have

- their cathode compartment filled with a graphite felt is the fact that because of the graphite felt the electrochemical processes take place in proximity to the electrolyte wall, and sulphur forms preferentially in the vicinity thereof. When the total solid electrolyte surface is covered with sulphur, Na_2S_5 located entirely in the cathode compartment can no longer contribute to the electrochemical conversion. The capacity of such a storage cell thus becomes so reduced that the basic advantage of a high energy content is to a large part lost. In the case of storage cells with high current densities, as designed for driving electric vehicles and for covering the peak loads in the electrical mains system, rapid and very efficient recharging is of particular importance.
- 30 The invention seeks to provide an electrochemical storage cell in which the internal resistance is less influenced by insulators which form in the cathode compartment, and which at the same time improves rechargeability.
- 35 According to the present invention, the additive is expanded graphite, mixed with sulphur.
- 40 The expanded graphite which is here disposed in the cathode compartment as the additive may be produced by special treatment from natural graphite. Natural graphite consists of carbon disposed in layers, which in contrast to the strong bonding forces within the planes of stratification are held together only by weak van der Waals forces. In characterising this bonding anisotropy, the orientation directions within the planes of stratification are indicated by 'a' axes and those which extend perpendicular thereto by 'c' axes. The various graphites, namely natural graphites, kish graphite and synthetic graphites (pyrolytic graphites) often possess very different degrees of orientation with respect to their structure, and thus show very different properties during their processing.
- 45 Graphites with a high degree of orientation such as natural graphites, can be processed so that the interspace between the overlying carbon layers becomes considerably enlarged, to produce an elongation in a direction perpendicular to the layers, i.e. in the c-axis direction. The layer-like structure remains substantially unaltered in the graphite with has been expanded or elongated in this manner.
- 50 In order to produce this expanded graphite particles are oxidised at a determined temperature for a given time. Suitable oxidising agents for this process are mixtures of sulphuric acid and nitric acid or mixtures of nitric acid and potassium chlorate. After oxidation, the graphite particles are washed with water and then heated to a temperature of between 350 and 600°C, in order to elongate the graphite particles in the direction of the c-axis as much as possible. At the end of this

process, graphite particles are obtained which have been elongated up to 25 times the original thickness. The graphite expanded in this manner can be further processed, without the addition of bonding agents, to form moulded bodies of graphite of which the material properties are independent of the type of initial material and show a good reproducibility. Because of the relatively simple method of producing the expanded graphite, as described heretofore, this represents a price advantage over all previously used materials for the sulphur electrode of the sodium/sulphur storage cell.

Advantageously, in one embodiment of the electrochemical storage cell according to the invention, a mixture is fed into the cathode compartment consisting of 50 to 98 ± 0.5 weight % of sulphur and 2 to $50 \pm 0.5\%$ of expanded graphite. A preferred mixture comprises a proportion of 85 – 95% sulphur, the proportion of expanded graphite then being between 5 and 15% . The mixture of sulphur and expanded graphite has a fluid character, possesses sufficient conductivity, and shows no tendency towards phase separation. Because of the fluid character of the mixture, it is possible to produce the sulphur electrode by casting such a mixture into an already assembled cell. The mixture is fed in preferably at a cell temperature of 130°C . As the sulphur electrode together with the expanded graphite can be fed into the already assembled storage cells, the production of the cells becomes considerably facilitated, so that a shorter production time is required for their manufacture, or alternatively a larger number of storage cells can be produced.

Advantageously, the graphite used for producing the storage cell can be placed into the cathode compartment with various degrees of precompression so that the conductivity and porosity can be adjusted over a wide range. The surface properties of the material change only slightly by doing this. A hollow cylinder can also be firstly cast from the fluid mixture, and then inserted into the cathode compartment.

According to a preferred feature of the invention, a hollow cylinder pressed out of sulphur and expanded graphite is inserted into the cathode compartment, the proportion of sulphur being 90 weight % and the proportion of expanded graphite being 10% .

According to a further embodiment of the invention, a pressed piece made of expanded graphite is inserted into the cathode compartment, and then impregnated with sulphur.

By using expanded graphite as the additive in the cathode compartment, substantial optimisation of the sulphur electrode in terms of the internal resistance and rechargeability becomes possible, as the specific resistance of this material can be adjusted over a wide range by corresponding compression.

The invention will now be described further, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a section through a storage cell of the invention, and

Figure 2 is a graph showing the variation of the resistance with the concentration of the expanded graphite.

Fig. 1 shows the storage cell 1 according to the invention, comprising a cup-shaped casing 2 of metal, a solid electrolyte 3 and a current collector 4. The cup-shaped metal casting is a tube closed at one end, and constructed of thin-walled aluminium or V4A steel. Other materials may alternatively be used for constructing the cup-shaped casing. The only consideration necessary in the choice of material is that it is corrosion-resistant to alkali metal polysulphides, in particular sodium polysulphides.

At its upper end, the cup-shaped casing 2 is provided with a flange 5 extending both inwards and outwards, and comprising bores for screws. The solid electrolyte 3, likewise of cup-shape, is disposed in the interior of the cup-shaped casing tube closed at one end. The dimensions of the solid electrolyte 3 are so chosen that between its outer surfaces and the inner surfaces of the cup-shaped casing 2 there is a minimum gap of a few millimetres overall, to form a continuous interspace 7. The interior of the solid electrolyte 3 serves as the anode compartment 8, in which the alkali metal, in particular sodium, is placed. The quantity of sodium to be placed in the solid electrolyte 3 is so chosen that the lower and lateral surfaces of the solid electrolyte are wetted with sodium. By means of an additional storage reservoir 9 for sodium disposed above the solid electrolyte 3, and which is connected to the solid electrolyte by way of an opening 10, the solid electrolyte 3 is always filled with sodium to a uniform level.

The solid electrolyte is provided at its open end with an outwardly extending flange 11, which rests by way of a gasket 12 on the flange 5 of the cup-shaped casing 2. The upper opening of the solid electrolyte is closed by means of an annular disc 13. This is constructed of a ceramic or other non-conducting material, and lies by way of a gasket 12 on the flange 11 of the solid electrolyte 3. The inner opening 10 of the annular disc 13 forms the connection between the solid electrolyte and the storage reservoir 9.

The storage reservoir 9 is also a tube closed at one end and constructed of metal or another material resistant to corrosion by sodium. The diameter of the storage reservoir 9 is chosen equal to the diameter of the opening 10 in the annular disc 13 of the solid electrolyte 3. At its open end, the storage reservoir 9 is provided all round with a flange 14 which is bent downwards at its edge such that it encloses part of the cell closure portion.

In order to firmly close the storage cell, the flange 14 and the flange 5 of the cup-shaped container 2 are provided with bolts which are aligned with each other. Screws 15 are screwed into the bolts in order to firmly close the storage cell.

A graphite rod which projects into the solid electrolyte 3 and passes through the storage reservoir 9, and of which the upper end projects outwards beyond the storage reservoir 9, acts as the anode current collector 4. The interspace 7 between the cup-shaped container 2 and the solid electrolyte 3 serves as the cathode compartment in this embodiment of the electrochemical storage cell and is filled with the sulphur, which serves as the catholyte.

In order for the electrochemical storage cell to be able to be again charged to its maximum charge capacity after discharge, an additive is fed together with the sulphur. In the embodiment of the electrochemical storage cell according to the invention, the additive is in the form of expanded graphite. Particularly advantageous for reducing the internal resistance of the storage cell is a filling of 85 weight % of sulphur together with a proportion of 15% of expanded graphite. This mixture produces a substantial reduction in the internal resistance of the storage cell. In using sulphur and expanded graphite as the cathode compartment filling, in order to attain optimum conditions in each case, as much sulphur and expanded graphite must be fed as is necessary to fill the cathode compartment completely. Good rechargeability of the storage cell is attained if 97 ± 0.5 weight % of sulphur and 3 ± 0.5 weight % of expanded graphite are contained in the cathode compartment. In all cases, the proportion of sulphur should be 50 to 98 weight %. The cathode compartment is filled at 130°C . As the sulphur and expanded graphite mixture has a fluid character at this temperature, it can be easily fed into the cathode compartment. In particular, it is possible to assemble the storage cell completely, i.e. including its closure, and then only after assembling the cell to feed the fluid sulphur and expanded graphite mixture into the cathode compartment through the filling opening indicated in Fig. 1 by 16. The expanded graphite disposed in the cathode compartment as the additive sufficiently satisfies the conditions set for a material inserted into the cathode compartment for fulfilling the stated desired requirements. In particular, the graphite has a low specific electrical resistance of about $20 \text{ Ohm m}^2/\text{m}$. The resistance of the expanded graphite can be simply adjusted by means of the concentration of the expanded graphite flakes, as can be seen in Fig. 2. On compression, the individual particles become oriented because of their anisotropy perpendicular to the direction of force (parallel to the stratification), so

that for an apparent density of the expanded graphite of about 0.5 g/cm^3 , corresponding to a porosity of about 75%, the specific electrical resistance is about $20 \text{ Ohm m}^2/\text{m}$.

If the particular situation requires it, the fluid mass consisting of molten sulphur and expanded graphite can be cast into a hollow cylinder form before its insertion into the cathode compartment. The dimensions of the hollow cylinder must then correspond to those of the cathode compartment. After the mass sets, the moulded body formed in this manner can be inserted into the cathode compartment.

Instead of feeding in the said fluid mixture of sulphur and expanded graphite, it is possible to prepare a porous pressing from the expanded graphite flakes, and to impregnate this with molten sulphur. The dimensions of the pressing are in this case chosen so that it completely fills the cathode compartment. Only the space between the floor of the solid electrolyte and the floor of the cup-shaped casing 2 can remain free. Preferably, a pressing having a density of 0.5 to 0.3 g/cm^3 is inserted into the cathode compartment. The pressing can alternatively be impregnated with the molten sulphur after its insertion into the cathode compartment, the molten sulphur then being fed into the cathode compartment through the filling opening 16 after closing the storage cell. The quantity of molten sulphur to be fed into the cathode compartment to impregnate the pressing can be exactly determined. In particular, it can be determined from the equation for determining the volume of the cathode compartment. This equation, for a maximum operating temperature is as follows:

$$V_K = 1.5 \frac{m(S)}{\rho(\text{Na}_2\text{S}_3)} + \frac{m(C)}{\rho(C)}$$

In this equation, V_K is the volume of the cathode compartment, $m(S)$ the mass of the inserted sulphur, $\rho(\text{Na}_2\text{S}_3)$ the density of Na_2S_3 at the maximum allowable temperature, $m(C)$ the mass of the expanded graphite and $\rho(C)$ the density of graphite at the maximum allowable operating temperature.

By solving the equation for $m(S)$, the sulphur quantity necessary for any cathode compartment can be determined. By means of this equation, the sulphur quantity to be fed into the cathode compartment can also be determined if, instead of a pressing, it is to be fed with a fluid mixture of sulphur and expanded graphite.

If it is not possible for production reasons to feed a fluid mixture of sulphur and expanded graphite at 130°C into the cathode compartment 7, it is possible to press a hollow cylinder from a mixture of powdered sulphur and expanded graphite flakes, and to insert this

into the cathode compartment. The quantity of powdered sulphur to be used can also be calculated from the aforesaid equation. Such a hollow cylinder can be inserted into the cathode compartment 7 at a temperature of 20°C. The dimensions of the hollow cylinder must be at least sufficiently large for the cathode compartment 7 to be completely filled. If using such a hollow cylinder, that region of the cathode compartment 7 lying between the floor of the solid electrolyte 3 and the floor of the cup-shaped casing 2 can remain free, without this being detrimental to the operation, in particular the rechargeability of the storage cell.

Expanded graphite can be used as the additive in the cathode compartment independently of whether the cathode compartment is located within the solid electrolyte 3 or in the interspace between the cup-shaped casing 2 and the solid electrolyte 3. The form in which the expanded graphite is fed into the cathode compartment 7, in particular whether it is fed in together with sulphur as a fluid mixture, or as a pressing which is then impregnated with sulphur, or as a hollow cylinder pressed out of powdered sulphur and expanded graphite flakes, is likewise independent of where the cathode compartment 7 is disposed inside the storage cell.

CLAIMS

1. An electrochemical storage cell based on alkali metal and chalcogen, comprising at least one anode compartment for holding the anolyte and a cathode compartment for holding the catholyte, these being separated from each other by an alkali ion-conducting solid electrolyte wall, an additive being placed into the cathode compartment for reducing the internal resistance and increasing the electrochemical reaction, wherein the additive is expanded graphite mixed with sulphur.
2. An electrochemical storage cell as claimed in Claim 1, in which 85 weight % of sulphur and 15% of expanded graphite are fed into the cathode compartment.
3. An electrochemical storage cell as claimed in Claim 1 or 2, in which a mixture consisting of 50 to 90% of sulphur and 2 to 50% of expanded graphite is fed into the cathode compartment.
4. An electrochemical storage cell as claimed in Claim 1 or 2, in which the fluid mixture of sulphur and expanded graphite is fed into the cathode compartment at a cell temperature of 130°C.
5. An electrochemical storage cell as claimed in any one of Claims 1 to 4, in which a hollow cylinder cast from a fluid mixture consisting of sulphur and expanded graphite is inserted into the cathode compartment.
6. An electrochemical storage cell as claimed in any one of Claims 1 to 4, in which a hollow cylinder pressed from powdered sulphur and expanded graphite flakes is inserted into the cathode compartment.

phur and expanded graphite flakes is inserted into the cathode compartment.

7. An electrochemical storage cell as claimed in Claim 6, in which the hollow cylinder contains 90 weight % of sulphur and 10% of expanded graphite.

8. An electrochemical storage cell as claimed in any one of Claims 1 to 4, in which a pressing of expanded graphite impregnated with sulphur is inserted into the cathode compartment.

9. An electrochemical storage battery comprising a plurality of cells as claimed in any preceding Claim.

10. An electrochemical storage cell constructed substantially as herein described with reference to and as illustrated in the accompanying drawings.

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